Dry reforming of ethane on tri-metallic perovskites ($LaCo_xFe_{1-x}O_3$). Characterisations and reactivity.

G. Rodriguez[1], A.C. Roger[1], L. Bedel[1], L. Udron[1], L. Carballo*, A. Kiennemann[1]*

[1]LMSPC-ECPM, UMR 7515 25, rue Becquerel 67087 Strasbourg Cedex 2 France

*Universitad National Colombia, Santa Fé de Bogota Colombia.

1. INTRODUCTION

The study of the catalytic dry reforming of light hydrocarbons (C_1, saturated C_2) is of interest for syngas (CO-H_2) production. The obtained CO-H_2 mixture can be used for hydroformylation, methanol or Fischer-Tropsch synthesis. The fast deactivation by excess of carbon deposits is the main drawback of metal supported systems (Ni, Co, Pt, Pd, Rh) [1]. Basic supports like MgO, La_2O_3 have been used to increase the catalyst live by lowering the rate of carbon deposition [2]. A second way has been explored through formation of well defined structure containing an active metal (nickel). For example, we have shown that the partial substitution of Ni by Fe in $LaNiO_3$ increases the Ni reduction temperature close to the reaction temperature. Strong Ni-tri-metallic perovskite interactions both improve lifetime and dispersion of nickel particles and decrease carbon formation and sintering of metal by formation of a Ni-Fe alloy [3,4,5]. Due to the good ability of perovskite-type oxides to be B-site substituted, Ni could be replaced by other metal such as Co.

The aim of the present study is to point out the interest of these defined Co-containing structures in reforming of ethane.

2. EXPERIMENTAL PART

2.1. Preparation. The mixed $LaCo_xFe_{1-x}O_3$ perovskites with x values varying from 0 to 1 (x = 0, 0.3, 0.5, 0.7, 1) were prepared from La acetate, Co acetate and Fe powder via a sol-gel related method [6]. The starting materials were separately dissolved in hot propionic acid under stirring and then mixed. After 30 minutes stirring, the boiling resulting solution was evaporated until a resin is obtained. This resin was heated 4 hours at 750°C with a ramping of 3°C.mn^{-1}. BET surface areas were in the range of 3 (x=0) to 6 m^2.g^{-1} (x=1).

2.2. Characterization The nature of the obtained phases and the lattice parameters were determined by powder X-Ray diffraction (XRD) recorded on a Siemens D-5000 diffractometer using the CuKα radiation.

Transmission electron microscopy (TEM) was performed on a TOPCON-EM002B apparatus coupled with an energy dispersive X-Ray device (EDS).

Temperature programmed reduction (TPR) was performed with a 50 mg sample placed in a U-shaped quartz tube (6.6 mm ID), the temperature was increased from 25 to 900°C with a slope of 15°C min^{-1}. The reducing mixture was 3 vol.% hydrogen in helium (50 mL min^{-1}). Hydrogen consumption was quantified by a TC detector after trapping on molecular sieve of the formed water.

2.3. Reaction conditions The operating conditions were the following : fixed bed quartz reactor (6.6 mm I.D.), inlet temperature : 400-800°C; feed flow rate : 0.15 L.h^{-1} ethane, 0.3 L.h^{-1} CO_2 and 2.55 L.h^{-1} Ar; catalyst amount: 100 mg. The outlet gas was analyzed by two on line gas chromatographs: one for C_2H_6, CO and CO_2; and a second one for CO and H_2.

3. RESULTS

3.1. Characterization of $LaCo_xFe_{1-x}O_3$ systems before catalytic test

XRD pattern of $LaCo_xFe_{1-x}O_3$ (x=0.3, 0.5 and 0.7) shows that a solid solution is formed in all proportions. A split of the main reflection line for x ≥ 0.5 is characteristic of the rhombohedral system (R) of $LaCoO_3$ isomorphs. Compounds without split reflection crystallize in the orthorhombic (O) system such as $LaFeO_3$ [7].

The different catalysts have been analysed by TEM-EDS to confirm the initial composition of the structures and the homogeneity of the preparation (figure 1).

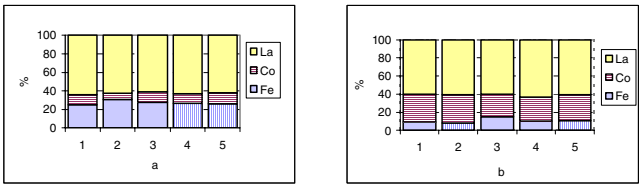

Figure 1. Elemental distribution observed by energy dispersive X-ray spectroscopy before catalytic test for: (a) $LaCo_{0.3}Fe_{0.7}O_3$ and (b) $LaCo_{0.7}Fe_{0.3}O_3$. (1) Broad focused beam 200nm (2-5) Narrow focused beam 14 nm.

The characterization (with broad and narrow focussed beam) shows a good homogeneity of each preparation which is formed of grains of around 50 nm each. The reducibility of the perovskites was studied by T.P.R.. The hydrogen consumption is given versus temperature for four different materials (figure 2).

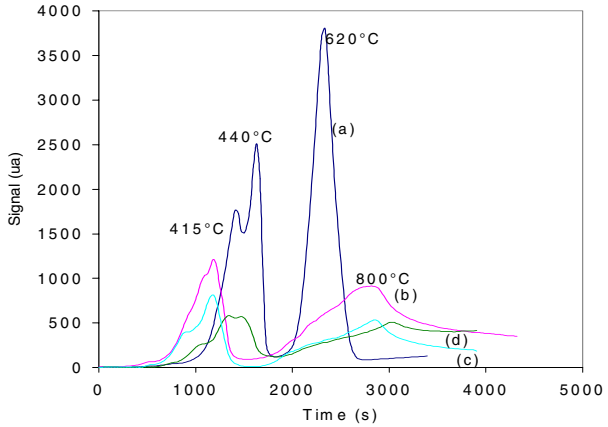

Figure 2. TPR before catalytic test for (a) $LaCoO_3$, (b) $LaCo_{0.7}Fe_{0.3}O_3$, (c) $LaCo_{0.5}Fe_{0.5}O_3$ and (d) $LaCo_{0.3}Fe_{0.7}O_3$.

The T.P.R. shape reveals two reduction areas. The first between 350°C and 500°C, the second with a maximum between 620°C ($LaCoO_3$) and 810°C ($LaCo_{0.3}Fe_{0.7}O_3$). The temperature of the second maximum increases with iron content. So it is possible to control the perovskite reduction temperature by varying the Co/Fe ratio, and to correlate it with the ethane reforming temperature.

3.2. Catalytic tests. Figures 3 and 4 show respectively the ethane conversion and the CO yield versus x for temperatures between 600°C and 800°C. Ethane conversion increases with increasing x values and temperatures. There is an important change in conversion and CO yield when x is equal or higher than 0.5. This value corresponds to a change of the structure from orthorhombic to rhombohedral. $LaCoO_3$ shows excellent results too, but deactivated very fast. On the other hand, catalysts containing cobalt and iron showed very good stability in addition to performance.

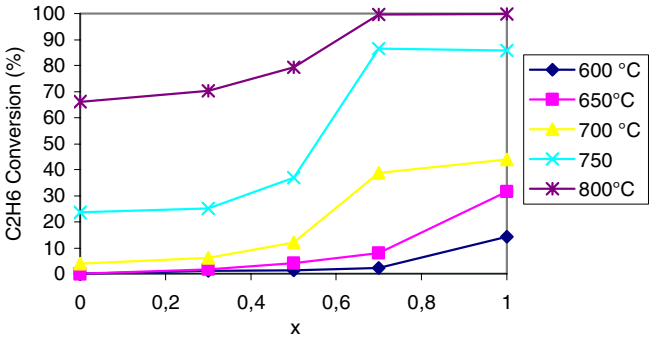

Figure 3. C_2H_6 Conversion at various temperatures versus x with a CO_2/C_2H_6=2 for $LaCo_xFe_{1-x}O_3$ perovskite.

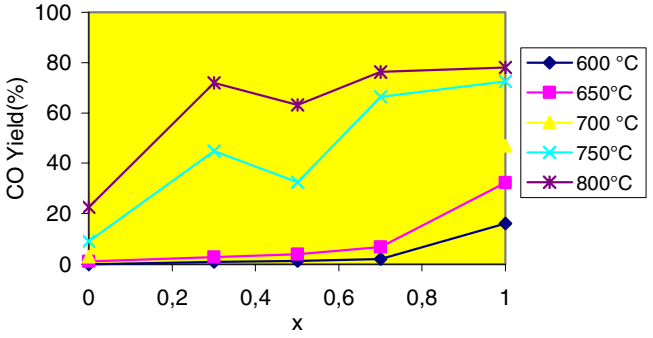

Figure 4. CO yield (%) at various temperatures versus x with a CO_2/C_2H_6=2 for $LaCo_xFe_{1-x}O_3$ perovskite.

The interest of the tri-metallic perovskite La-Co-Fe compared to the bi-metallic La-Co is better understood by characterization of the catalysts after test.

3.3. Characterization after test. XRD diffraction patterns after test show different phases depending on x values as summarised in Table 1.

x	Crystalline phases detected by XRD after catalytic test					
0	$LaFeO_3$					
0.3		$LaCo_wFe_{1-w}O_3$	La_2O_3			
0.5		$LaCo_zFe_{1-z}O_3$	La_2O_3			
0.7			La_2O_3	$LaFeO_3$	Co	
1			La_2O_3		Co	CoO

Table 1. Crystalline phases detected by XRD after test for $LaCo_xFe_{1-x}O_3$ perovskite oxides.

For higher cobalt contents (x > 0.5) the three-metal perovskite structure is destroyed and the most stable $LaFeO_3$ perovskite is formed together with lanthanum oxide and cobalt. $LaFeO_3$ perovskite could also be characterised by FT-IR (555 cm^{-1}). For low cobalt content, the La-Co-Fe perovskite is preserved, although cobalt content is less than in the initial structure.

The LaCoFe elemental distributions (EDS) are given in figure 5 and the La/Fe ratios in figure 6 for x = 0.3 and 0.7. Figure 5 shows a higher heterogeneity of $LaCo_{0.7}Fe_{0.3}O_3$ compared to $LaCo_{0.3}Fe_{0.7}O_3$. For x = 0.3, almost the same ratio La/Co/Fe or La/Fe are observed in different parts of the sample, no free cobalt has been seen confirming that the tri-metallic structure was preserved. However, analyses show clearly that part of cobalt has left the perovskite and w and z (Table 1) are lower than the initial value of x. For x = 0.7, the tri-metallic perovskite is destroyed, free cobalt particles are evidenced and the La/Fe ratio changed. The change in La/Fe ratio indicates the presence of free lanthanum (as oxide or hydroxide). In the latter case, in agreement with XRD results, it can be concluded that the $LaFeO_3$ perovskite behaves as a support for cobalt metal particles of 10 to 50 nm (TEM).

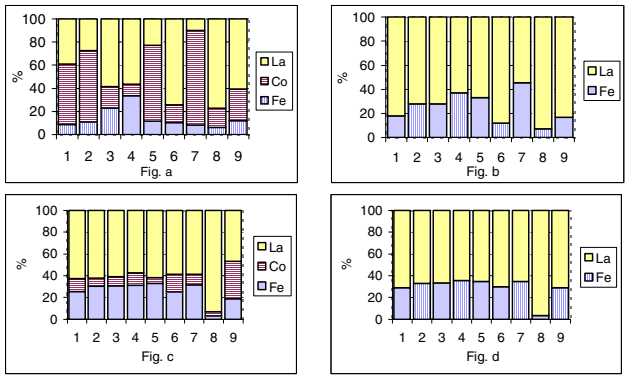

Figure 5. Elemental distribution observed by energy dispersive X-ray sprectroscopy after catalytic test for: $LaCo_{0.7}Fe_{0.3}O_3$ (a) La, Co and Fe. (b) La and Fe. $LaCo_{0.3}Fe_{0.7}O_3$ (c) La, Co and Fe. (d) La and Fe. (1) Broad focused beam 200nm (2-9) Narrow focused beam 14 nm.

4. DISCUSSION AND CONCLUSIONS

In the present study, we can see that whatever the x value (until 0.7), the perovskite structure is preserved : as LaCoFe for $x \leq 0.5$ and as a LaFe system for $x \sim 0.7$.

The catalytic results have shown an increase of reactivity with the increase of the x value and of the reaction temperature. Moreover a gap of activity corresponds to a change of the perovskite structure from orthorhombic to rhombohedral. Such a change has also been seen in Fischer-Tropsch reaction (7). Good aging for the catalysts suggests that coke formation is limited as confirmed by elemental analyses. Different explanations could be given : formation of small Co metal particles in strong interaction with the perovskite support or formation of a Co-Fe alloy and dilution effect. With La-Fe-Co catalysts alloy formation was not seen. For $0.3 \leq x \leq 0.7$, we suggest that the presence of cobalt inside the partially reduced perovskite network is in strong interaction with the free cobalt and then avoids an excessive coke formation, resulting in a good aging. This strong interaction is confirmed by the possibility of regeneration of the used catalyst by heating at high temperatures (900°C). Another contribution to decreasing coke formation is the performance of $LaFeO_3$ in total oxidation of hydrocarbons. Thus it is postulated that $LaFeO_3$ as well as La_2O_3 will participate in the oxidation of coke precursors.

Acknowledgement. The authors are deeply grateful to ECOS-NORD for providing fellowship to G. Rodriguez and to the European Community through the RUCADI program.

REFERENCES

(1) J.R. Rostrup-Nielsen, *Catalysis Science and Technology 5* **1984**, *1*, J.R. Anderson, and M. Boudart (eds) Springer (Berlin).
(2) F. Frusteri, F. Arena, G. Calogero, T. Torre, A. Parmaliana, *Catalysis Communications* **2001** *2* 49.
(3) H. Provendier, C. Petit, C. Estournes, S. Libs, A. Kiennemann, *Appl. Catal. A* **1999** *180* 163.
(4) C. Petit, A. Kiennemann, P. Chaumette, O. Clause, *U.S. Patent 5447705* **1995**.
(5) H. Provendier, C. Petit, C. Estournes, A. Kiennemann, *Stud. Surf. Sci. Catal.* **1998** *119* 741.
(6) H. Provendier, C. Petit, J.L. Schmidt, A. Kiennemann, C. Chaumont, *J. Mater. Sci.* **1999** *34* 4121.
(7) L. Bedel, A.C. Roger, A. Kiennemann, C. Estournes, Prepr. Pap. ~ *Am. Chem. Soc., Div. Petroleum Chem.*, **2000**, *45*, 236.